

CHEMISTRY OF COAL ASH MELTING IN GASIFICATION AND COMBUSTION

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INTRODUCTION

Coal deposits occur in a number of localities within the United States. The mineral matter in the coal varies with the location but is usually made up of quartz, pyrite, clay, shale and smaller amounts of other materials. The relative amounts of the mineral matter in the parent coal will vary from one region to another and within regions, as well as individual coal seams. During combustion or gasification, the mineral matter will contact other types of mineral matter resulting in a coal ash of different properties than the parent mineral species.

Our reliance on coal for production of energy via combustion or synthetic fuels will necessitate the ability to operate under a wide range of conditions. The boilers that generate electric power are in some cases designed to reject coal ash in the form of a molten slag. Some gasifiers are intended to operate with a continuous flow of molten ash from the gasifier to a collection zone. Continuing reliable operation of this equipment requires the ability to sustain an ash viscosity within a range to permit the ready removal of the ash material.

The determination of viscosity of the ash from coal is an expensive and time-consuming operation. A number of efforts have been made to correlate this property with the chemical composition. Different types of correlation have been suggested for use with coal ash of different ranges of compositions. It is desirable to have some understanding of the chemistry of the interactions that occur within the melt in order to more fully understand the melting behavior of this material and to make effective predictions of that behavior from the chemical composition.

ASH CATION PROPERTIES

The species that make up a coal ash after it has been in the reactor are usually metal oxides. This discussion assumes the coal ash materials are, or have been, converted to oxides. In a general way the behavior of the different ions can be viewed as the result of the important properties of charge and size that the positive ions or cations possess.

One of the more important properties is that of the size or radius. A listing of cation radii is given below for the important metal ion species in coal ash.

Si ⁺⁴	0.42	Fe ⁺²	0.74
Al ⁺³	0.51	Na ⁺¹	0.94
Fe ⁺³	0.64	Ca ⁺²	0.99
Mg ⁺²	0.67	K ⁺¹	1.33
Ti ⁺⁴	0.68		

These cation radii according to Ahrens (1) are given in angstrom units, Å (10^{-8} cm). The largest ion is roughly three times the size of the smallest.

A number of correlations of behavior have been made with the base-to-acid ratio of the oxide mixtures. The acids have been defined as oxides of Si, Al, and Ti. The bases have been identified as the oxides of Fe, Ca, Mg, Na, and K. The listing of radii does not readily divide the group into acids and bases. Iron is listed twice because it can occur in melts in two oxidation states.

In melts and other liquid solutions there is a tendency for the smaller more highly charged positive ions to draw the larger negatively charged ions into a complex ion. For coal ash this complex could have a general formula, MO_x^{-n} , where x oxide ions are coordinated around an M ion and the overall negative charge is n units. The coordination number, x, is determined primarily by the ratio of the radii of the M and O ions. The value of 1.40 angstroms was assigned to the oxide ion. A coordination number of 4 is observed for Si and Al. The coordination number of 6 is observed for the rest of the ions except K which has the number of 8 in these systems. In some cases Al may also be found with a coordination number of 6.

The other property of importance in the coal ash cations is that of charge. The charge affects the relative capacity to attract the negative ions to the cation. The capacity is also affected by the size of the ion. The ionic potential, defined as the ratio of cation oxidation state or valence to the ionic radius, gives a measure of the ability of the cation to attract the anion. A high ionic potential indicates an ability to compete effectively with other ions of lower ionic potential for a limited supply of oppositely charged ions. The values of the ionic potentials calculated from the ionic radii given earlier are listed below.

Si ⁺⁴	9.5	Fe ⁺²	2.7
Al ⁺³	5.9	Ca ⁺²	2.0
Ti ⁺⁴	5.9	Na ⁺¹	1.1
Fe ⁺³	4.7	K ⁺¹	0.75
Mg ⁺²	3.0		

Examination of these values quickly indicates that the highest values belong to the acid group of Si, Al, and Ti, while the lower values are associated with the bases. This grouping and the physical interpretation of the ionic potential lead to the suggestion that this parameter is a physical characteristic which can be useful in quantifying acid and base behavior. To the extent that this is true, then this parameter should also be useful in further efforts to correlate coal ash chemical compositions with melting, viscosity and other properties associated with ash deposition in the process.

The ionic potential is an indication of a cation's capacity to form a complex ion such as SiO_4^{-4} . This capacity may be limited by the availability of oxide ions as in coal ash systems. In the compound SiO_2 each Si is expected to have

four oxide ions around it. This can only be accomplished if oxygen ions are shared between different Si ions. This tetrahedral coordination occurs both in the solid and liquid state and requires sharing of oxide ions in all cases. The sharing of oxide ions leads to the formation of polymeric aggregates in the liquid state. Individual angular SiO_2 groups may join in chains, sheets, or other arrangements. These groupings require additional oxide ions for termination of the polymer. Oxides of ions of lower ionic potential than Si can provide these oxide ions. The groupings will terminate more frequently and the average polymer or aggregate size would decrease as more oxide ions became available. Al ions occur in many mineral species with Si and are able to take the place of Si in the polymeric groupings. In a similar fashion it is expected that they would be able to participate in the polymer formation in the melt. Alkali metal oxides could most readily supply oxide ions since they have the lowest ionic potentials. The alkali cations would find positions between the polymeric chains or other groupings involving Si and Al. At equilibrium, complexes will be formed due to attractive forces and disrupted by thermal energy. A population of complexes of various sizes would be expected for a given composition. The larger the aggregates, especially chain types, the greater the number of opportunities for interaction between them and to increase the viscosity.

The effectiveness of the addition of other cations to reduce the viscosity for reliable slag formation depends on the rate of mixing of the additives, the dissociation of the cations and oxide ions and the diffusion of these ions into the melt. These steps are typically much slower than the acid-base reaction in water solutions typified by titration.

A flux such as fluorite, CaF_2 , is added in some cases to decrease the viscosity of a melt. This material provides a supply of anions with a size comparable with oxide ions. The fluoride radius is 1.36 Å compared to 1.40 for oxides. Fluorite is even more electronegative than oxide and both can serve as chain terminators. The addition of calcium fluorite instead of the oxide provides twice as many anions for each calcium ion, effectively doubling the capacity to limit polymer formation.

In coal ash melts, the role of an acid is that of a complex ion or polymer former. The tendency for polymer formation increases with ionic potential. The bases serve as oxide ion donors. The tendency to yield oxide ions is greatest for those with lowest ionic potential. The oxide ions are attracted by cations with the highest ionic potential in the system to form polymers, terminate polymer groupings and diminish viscosity. The cations with low ionic potentials exist as unattached hard spheres and can facilitate slippage between the polymer groups.

THE ROLE OF IRON

Ferric and ferrous ions have significantly different ionic potentials (4.7 and 2.7). The ferric ion falls between the values for the acid group and the basic group. The importance of iron is associated with its unique ability to alternate between the two valence states, the different behavior associated with

each state and its significant contribution to the composition of many coal ashes. Iron acts as either an acid or a base depending on its charge. The intermediate values for ionic potential indicates that ferric iron would be a weak acid and ferrous would be a moderate base.

The combustion process in boilers produces a coal ash with a mixture of the two states. Analyses have indicated that about 20% is present as ferric ion while the remainder was ferrous. In some slagging gasifiers elemental iron has been observed. Since the majority of the iron was present as ferrous ion it was appropriate to classify the iron oxides with the bases (assuming that a single classification had to be made) even though the oxide is identified as Fe_2O_3 in earlier correlations. The gaseous environment determines the equilibrium oxidation state of the iron in coal ash systems. Iron is an important component of most Eastern coal ashes, usually following Si and Al in abundance. The behavior of the coal ash system depends on the oxidation state of the iron. Viscosity studies show a reduction of coal ash viscosity for reducing conditions with a reduction of the ratio of ferric to ferrous iron. (2) This observation is consistent with the role of a complex former for the acidic ferric iron and an oxide donor role for the ferrous iron.

Figure 1 (3) indicates the liquidous relationships in the alkali and alkaline earth-silica systems. A comparison of the depression of the melting point for different alkali metal oxides indicates that the depression is greatest for the ions with lowest ionic potential or strongest bases. A similar relationship holds for the alkaline earths. In general, for this series of bases the melting point depression increases with decreasing ionic potential.

Table 1 (4) indicates the analysis of a series of coal ashes and gives the ash fusion temperatures. The indicated initial deformation temperature of 2900°F is just below 1600°C for the low-volatile bituminous coal. This material is essentially a two-thirds SiO_2 /one-third Al_2O_3 mixture. An examination of the Al_2O_3 - SiO_2 equilibrium diagram indicates that this softening temperature would be close to the eutectic melting temperature. One would then expect a very much higher liquid temperature.

Table 1 also gives the ash analyses of a series of high-volatile bituminous coal taken from three Eastern fields and one Western field. The SiO_2 contents of three of the four are close to 48%. The Al_2O_3 contents diminish from about 23% to 11%. The TiO_2 remains relatively constant in the range 0.6 to 1.0%. The Fe_2O_3 content is indicated from about 29.3 down to 7% which would indicate a wide range of behavior depending on the gaseous environment. The sum of SiO_2 and Al_2O_3 , the dominant acid species, is greatest for the Ohio coal and the highest oxidizing fluid temperature is observed for this material. The next highest sum is for the Illinois coal and this one has the next highest oxidizing fluid temperature. The remaining two (Utah and West Virginia) have similar total Si and Al contents. However, the iron content is much lower for the Utah coal than for the West Virginia coal. In an oxidizing environment this means that the total acid content would be higher for this coal and a higher oxidizing fluid temperature is observed for the West Virginia fuel.

An examination of the phase equilibrium diagram for the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$, Figure 2 (5), shows that in the region of about 50% SiO_2 , 25% Al_2O_3 , 25% FeO , which corresponds fairly closely to the Ohio coal, one would expect a liquidus temperature of about 1450°C (2642°F) which is in good agreement with the fluid temperature in the reducing environment for the Ohio coal ash. The lowest temperature on the diagram is at the eutectic between fayalite, tridymite and iron cordierite. The indicated temperature is 1083°C or 1980°F which is in general agreement with the observed initial deformation temperature for the reducing environment. The minimum temperature would correspond to a localized region in a sample where this phase could form through diffusion of different constituents with the required composition for formation of that material.

The composition of the Illinois coal ash is similar; however, this material does contain a significant amount of calcium oxide which is expected to reduce the melting temperature below that observed for the Ohio coal. The two temperatures are similar but are somewhat less for the Illinois material.

The West Virginia coal is richer in Fe_2O_3 according to the analysis. Again, referring to the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ phase equilibrium diagram and normalizing the content of these three constituents, the material falls in the same general region in the phase diagrams as the Ohio and Illinois coals. However, the melting temperature expected appears to be about 1540°C or about 2430°F . This temperature is somewhat higher than the observed reducing fluid temperature, however there is also about 4% calcium oxide, 1.2% magnesium oxide, and smaller amounts of other bases which contribute to the reduction in observed temperature.

The observed reducing initial deformation temperature is similar for the three coals from Ohio, West Virginia and Illinois. The same equilibrium phase diagram would apply to all three and would reflect the earlier mentioned minimum temperature.

The Utah coal is richest in SiO_2 , CaO , and Al_2O_3 . In the phase equilibrium diagram for this system, Figure 3 (6), the normalized composition for this ash lies in the pseudo-wollastonite region. From this normalized composition the melting temperature to be expected is about 1280°C or 2336°F . The solid species would be a wollastonite ($\text{CaO} \cdot \text{SiO}_2$). This temperature is about 80° above the observed fluid temperature in a reducing environment, indicating that the iron has the ability to depress the melting point by this amount in conjunction with the other basic materials. The oxidation of the iron is able to elevate the fluid temperature as indicated, through production of the acid ferric ions and associated change in oxide ion availability.

BIBLIOGRAPHY

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3. *Phase Diagrams for Ceramists*, E. M. Levin, H. F. McMurdie & F. P. Hall, Fig. 128, pp. 66 (1956). Am. Ceram. Soc., Columbus, Ohio.

4. Ref. 2, pp. 15-20.
5. Ref. 3, Fig. 696, pp. 241 (1964 edition).
6. Ref. 3, Fig. 631, pp. 220 (1964 edition).

Table 1

Ash content and ash fusion temperatures of some U.S. coals

Rank:	Low Volatile Bituminous	High Volatile Bituminous			
Seam	Pocahontas No. 3	No. 9	Pittsburgh	No. 6	
Location	West Virginia	Ohio	West Virginia	Illinois	Utah
Ash, dry basis, %	12.3	14.10	10.87	17.36	6.6
Sulfur, dry basis, %	0.7	3.30	3.53	4.17	0.5
Analysis of ash, % by wt					
SiO ₂	60.0	47.27	37.64	47.52	48.0
Al ₂ O ₃	30.0	22.96	20.11	17.87	11.5
TiO ₂	1.6	1.00	0.81	0.78	0.6
Fe ₂ O ₃	4.0	22.81	29.28	20.13	7.0
CaO.....	0.6	1.30	4.25	5.75	25.0
MgO.....	0.6	0.85	1.25	1.02	4.0
Na ₂ O.....	0.5	0.28	0.80	0.36	1.2
K ₂ O.....	1.5	1.97	1.60	1.77	0.2
Total.....	98.8	98.44	95.74	95.20	97.5
Ash fusibility					
Initial deformation temperature, F					
Reducing.....	2900+	2030	2030	2000	2060
Oxidizing.....	2900+	2420	2265	2300	2120
Softening temperature, F					
Reducing.....		2450	2175	2160	
Oxidizing.....		2605	2385	2430	
Hemispherical temperature, F					
Reducing.....		2480	2225	2180	2140
Oxidizing.....		2620	2450	2450	2220
Fluid temperature, F					
Reducing.....		2620	2370	2320	2250
Oxidizing.....		2670	2540	2610	2460

$\text{SiO}_2\text{-R}_2\text{O, RO}$

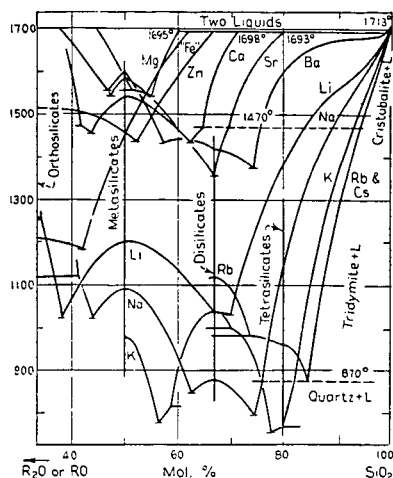


Figure 1. Liquidus Relations in the Alkali and Alkaline Earth-Oxide- SiO_2 Systems

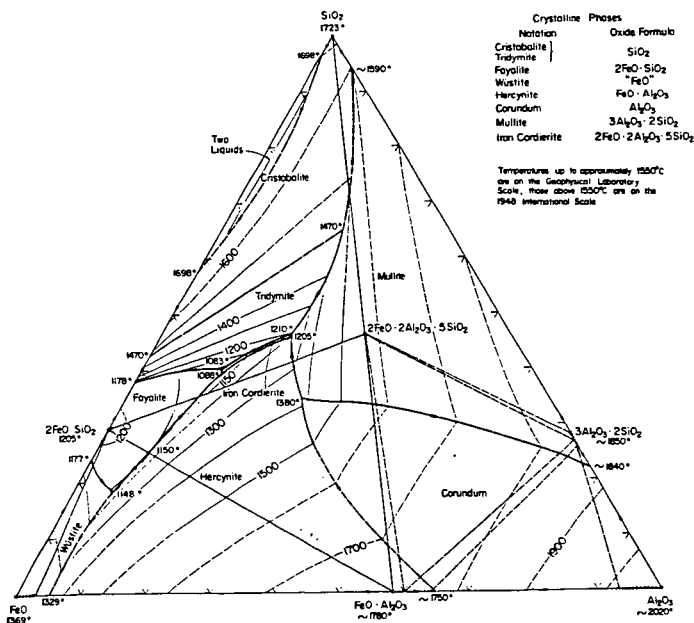


Figure 2. Composite "FeO"- Al_2O_3 - SiO_2 System

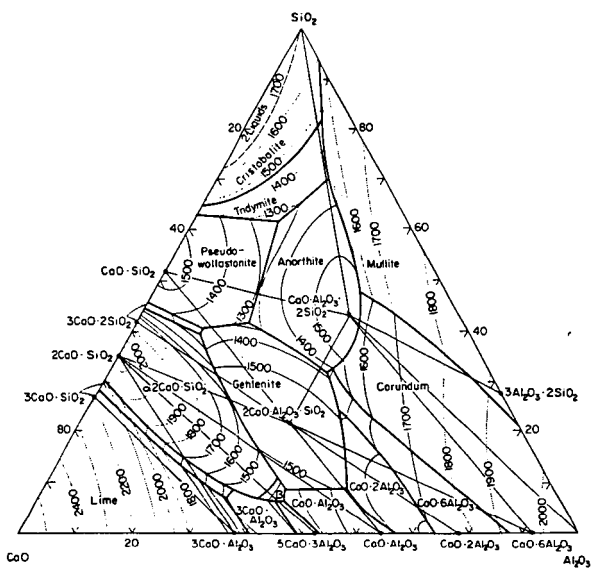


Figure 3. $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ System